Atomic-scale Observation of Polarity in Epitaxial Ferroelectric Thin Films

An x-ray diffraction method based on the excitation of an x-ray standing-wave field inside a film that directly senses the phase of the structure factor is demonstrated and used for determining the local polarity of thin ferroelectric films. The method is used to sense the displacements of the Pb and Ti sublattices in single-crystal c-domain $PbTiO_3$ thin films grown by metal-organic chemical vapor deposition on $SrTiO_3$(001) substrates. A study of the ferroelectric thin films that were poled "up" or "down" by an externally applied electric field has also been conducted.

Ferroelectricity in solids originates from the relative shifts of the anion and cation atomic sublattices [1], resulting in a net dipole moment (spontaneous polarization) along a certain crystallographic axis. Under an applied electric field, the direction of the polarization vector can be switched. This bistable property, in conjunction with thin-film heteroepitaxy, provides the basis for the development of a new type of nonvolatile random access memory [2]. Figure 1 depicts the polarized "up" and "down" unit cells for the ferroelectric $PbTiO_3$ perovskite structure (used in this study) with opposite dipole moments along the [001] polar axis due to the displacements of the Pb^{2+} and Ti^{4+} sublattices with respect to the O^{2-} sublattice. Electrical and piezo-response measurements are typically used to study such structures on a macroscopic scale. However, such measurements do not provide unambiguous insight into the atomistic processes underlying the polarization switching process. At the Advanced Photon Source, we have developed a thin-film x-ray standing wave (XSW) method to probe the polarity of ferroelectric thin films on an atomic scale [3] and furthermore to observe polarization switching in ferroelectric capacitor structures [4].

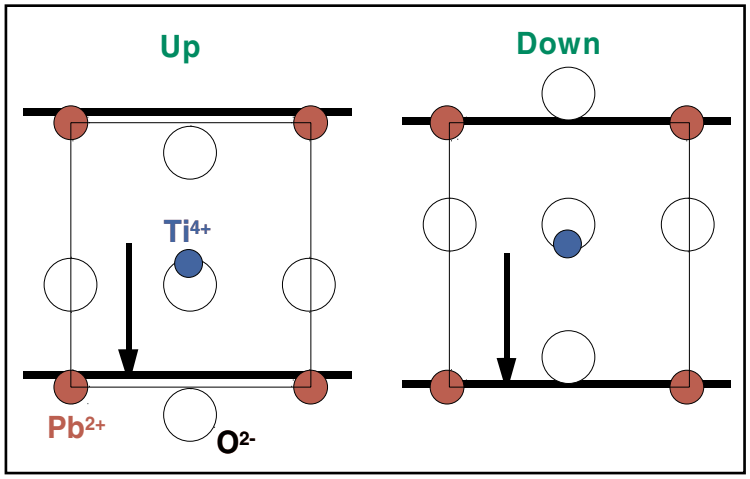

FIG. 1. The a-axis projection of the noncentrosymmetric $PbTiO_3$ tetragonal "up" and "down" perovskite unit cells. The thick solid lines represent the (001) diffraction planes. The arrow marks the inward path that the XSW antinode follows as θ increases from the low- to the high-angle side of the (001) Bragg reflection. In the $Pb(Zr_xTi_{1-x})O_3$ (PZT) solid solution, Zr^{4+} randomly substitutes for Ti^{4+}.

In a traditional XSW experiment, the XSW is generated by a strong Bragg reflection from a bulk perfect single crystal [5]. The outgoing diffracted plane wave interferes with the incident plane wave and forms a standing wave field. This standing wave field has the same periodicity as the diffraction planes. As the crystal is advanced in angle through the arc-second-wide "total reflection," the antinodes of the standing wave field shift from a location halfway between the diffraction planes to a position coincident with the planes. This inward shift of the antinodes causes an angle-dependent modulation in an atom's fluorescence signal that can be used to determine that atom's lattice position(s). This traditional method is not, in general, applicable to thin-

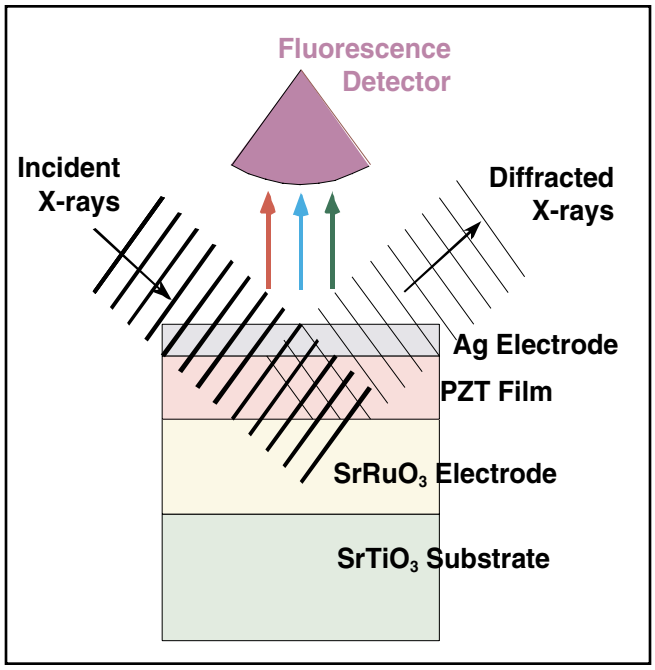

FIG. 2. A side-view depiction of the layers within the PZT capacitor structure starting with a $SrTiO_3$ (001) single crystal substrate, followed by a 136-nm-thick "single crystal" $SrRuO_3$ bottom electrode, a 20-nm-thick "single crystal" PZT film, and a polycrystalline 30-nm-thick Ag top electrode. [The $PbTiO_3$ / $SrTiO_3$ (001) heteroepitaxial structures were grown without the two electrode layers.] For the thin-film XSW measurements, the incident angle is tuned to the PZT or $PbTiO_3$ (001) Bragg peak, and the weak standing-wave field is generated inside the diffracting film by the interference between the very intense incident plane wave and the very weak diffracted plane wave. The XSW antinodes have the same periodicity as the (001) diffraction planes. An energy-dispersive solid-state detector is used to monitor the atom-specific x-ray fluorescence signals from the heterostructure.

film overlayers, since the period of the atomic layers in the film would not, in general, be equal to the period of the XSW probe generated by the substrate diffraction planes. For this case, we generate the XSW by the weak kinematical Bragg diffraction from the film itself, as depicted in Fig. 2. Since the thin-film reflection will be weak, the modulation in the fluorescence signal will also be weak. Therefore a high-intensity x-ray source, such as an APS undulator, is required to observe this phenomenon with the required counting statistics to extract atomic-scale structural information from the analysis of the data.

The first ferroelectric system examined by the thin-film XSW technique was $PbTiO_3$. PTO films of 10 nm, 20 nm, and 40 nm were grown on single-crystal $SrTiO_3$ (001) substrates by metal-organic chemical vapor deposition (MOCVD). The (001) XSW data for the 40-nm film are shown in Fig. 3.

Both the Pb L and Ti K fluorescence signals were monitored while scanning through the PTO (001) Bragg peak. The Pb signal was collected at an incident beam energy of 13.5 keV and the Ti signal at 8.0 keV. To collect Ti fluorescence from the $PbTiO_3$ film but not from the $SrTiO_3$ substrate, fluorescence slits were employed to take advantage of the evanescent-wave technique. Note that the Pb and Ti modulations are roughly counter-phase,

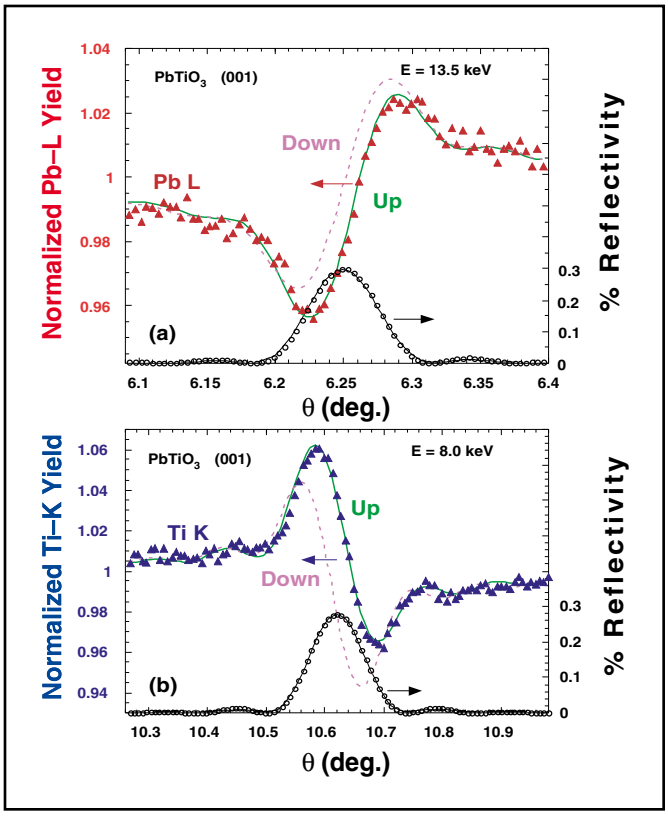

FIG. 3. The experimental XSW data measured from a 40-nm-thick $PbTiO_3$ film. (a) The angle θ dependence of the normalized Pb L fluorescence yield and reflectivity at the $PbTiO_3$ (001) reflection at an incident energy of 13.5 keV; (b) the Ti K fluorescence yield and reflectivity at the $PbTiO_3$ (001) reflection at 8 keV. The best fits for the "up" and "down" polarities are shown as solid and dashed lines, respectively. From Ref. 3.

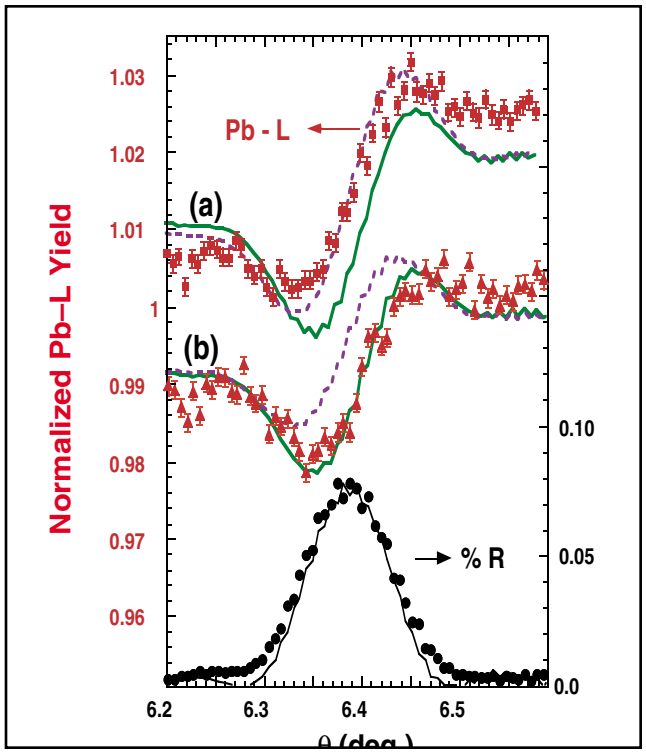

FIG. 4. The experimental XSW data measured from a 20-nm-thick PZT (001) film that had been polarized (a) "down" and (b) "up" at the completion of its hysteresis loop. The data consist of the angle θ dependence of the normalized Pb L fluorescence yield and reflectivity in the vicinity of the PZT (001) reflection at an incident energy of 13.50 keV. The best fits for the "up" and "down" polarities are shown as solid and dashed lines, respectively. The yield data and theory curves for (a) "down" have been given a 0.02 vertical offset for purposes of clarity. From Ref. 4.

because the Pb and Ti atomic planes are separated by approximately one-half of a PTO (001) diffraction plane spacing (see Fig. 1). On the low-angle side of the rocking curve, the antinodes start approximately on the Ti planes. As the crystal is rocked through the (001) reflection, the antinodes travel inward toward the Pb planes. Thus, the Ti signal peaks on the low-angle side and the Pb signal peaks on the high-angle side of the rocking curve. Based on the direct connection between the phase of the XSW and the phase of the structure factor, it can be shown that the antinodes should pass through the Ti planes, but not the Pb planes, for the "up" case, whereas the opposite should be true for the "down" case. The theoretical fitted curves in Fig. 3 for the two models clearly show this behavior and indicate that the 40-nm as-grown PTO film is polarized up. With a 0.5-mm x-ray footprint on the sample, other lateral positions on this particular film were examined, and all were found to be polarized "up". Other PTO films examined by this method were found to have some domains polarized "up" and some "down." We suspect that the resulting polarity of these as-grown PTO domains is directly linked to the atomic (Sr or Ti) termination of the topmost atomic layer of the substrate.

As a next step, we proceeded to examine ferroelectric thin films that were poled "up" or "down" by an externally applied electric field. The $Pb(Zr_{0.3}Ti_{0.7})O_3$ (PZT) ferroelectric capacitors used in this study [4] are illustrated in Fig. 2. The x-ray beam footprint was confined to an individual top Ag electrode that had a lateral dimension of 0.25 mm. The top electrode of a selected capacitor was connected to the output voltage of a function generator, while the bottom electrode was held at ground. As the bias voltage was cycled, the current was measured in order to monitor the ferroelectric-switching behavior. Some capacitors showed hysteresis loops that were shifted off-center in voltage, suggesting the existence of a "hard" and an "easy" state of polarization. This phenomenon is generally referred to as imprinting. For our particular capacitors, this imprinting phenomenon may be due to the manner in which the PZT films grow on the $SrRuO_3$ bottom electrode layers and to the asymmetry in the heterostructure. The thin-film XSW analysis of two different PZT capacitors (one poled "down" and one poled "up") are shown in Fig. 4.

These results demonstrate how x-ray standing waves can be used to probe the atomic-scale structure of electrically switched ferroelectric thin film/electrode heterostructures. The success of this type of measurement opens the door to more complex endeavors. For example, by combining the thin-film x-ray standing wave method with x-ray microfocusing and *in situ* biasing, one could observe real-time switching with micrometer-scale lateral resolution. Therefore, not only the static structure but also the dynamics of thin-film ferroelectric switching can be studied with this method.

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